

**BEFORE THE DIRECTOR OF THE  
DEPARTMENT OF PESTICIDE REGULATION  
STATE OF CALIFORNIA**

**In the Matter of the Responsible Farmers Coalition's**  
Request for Approval of  
Reduced Volatile Organic Compound  
Emissions Field Fumigation Methods

**DECISION**

**(California Code of Regulations, Title 3, section 6452)**

**RESPONSIBLE FARMERS COALITION**

**Mr. John Guerard**  
**c/o Bolthouse Farms**  
**7200 East Brundage Road**  
**Bakersfield, California 93307**

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**Summary**

The Responsible Farmers Coalition submitted a study to the Department of Pesticide Regulation (DPR) titled "Field Volatility of MITC After Application of Metam-Sodium by Chemigation and Shank Injection Comparing Standard Water Sealing and Pulsed Water Sealing" dated October 18, 2007. As part of DPR's efforts to reduce volatile organic compound (VOC) emissions, most night applications of methyl isothiocyanate (MITC)-containing pesticides are prohibited within several ozone nonattainment areas (NAAs) during May–October, under Title 3, California Code of Regulations (3 CCR) section 6450.1(c). However, the regulations also include a provision for the DPR Director to grant interim approval of fumigation methods that reduce VOC emissions (3 CCR section 6452). DPR has completed its evaluation of the two fumigation methods described in the study as specified in 3 CCR section 6452. The submitted study indicates high uncertainty as to exact emissions for the two methods. Despite the uncertainty of the data, DPR has determined that the methods meet the ultimate test for approval as interim methods, as described below. Effective May 1, 2008, DPR grants approval for interim use of the shallow shank injection method described in the study in all five ozone NAAs. Effective May 1, 2008, DPR grants approval for interim use of the sprinkler method described in the study for the Sacramento Metro and South Coast ozone NAAs, but not the San Joaquin Valley, Southeast Desert, or Ventura ozone NAAs during May–October. The emission ratings assigned to these methods will be equal to the highest rating for any currently approved method for metam-sodium in each specific area. The methods described in the study may be used for three years from the effective date, contingent on the submittal of an additional study to more accurately document the emissions from these fumigation methods.

## **Background**

VOCs contribute to the formation of ozone, a major air pollutant in several regions of California. Under the federal Clean Air Act, California's State Implementation Plan for ozone includes an element to track and reduce VOC emissions from pesticides. On January 25, 2008, DPR adopted regulations to control VOC emissions from fumigants during the May–October peak ozone season in five ozone NAAs: Sacramento Metro, San Joaquin Valley, Southeast Desert, South Coast, and Ventura.

The Responsible Farmers Coalition submitted comments for DPR's regulations during the rulemaking process. During this rulemaking process, DPR modified its originally proposed text and provided the public an opportunity to comment on the modifications. As part of their comments, the Responsible Farmers Coalition included a study on field emissions from several experimental applications of metam-sodium at night, "Field Volatility of MITC After Application of Metam-Sodium by Chemigation and Shank Injection Comparing Standard Water Sealing and Pulsed Water Sealing" dated October 18, 2007. This study and comments on night applications of metam-sodium were not relevant to the modifications, and therefore, no revisions to the regulations were considered at that time. DPR has since adopted the regulations, including a provision prohibiting most night applications of MITC-containing pesticides [3 CCR section 6450.1(c)]. However, the regulations also include a provision for interim approval of fumigation methods with emissions no greater than the field fumigation methods allowed in the regulations in the respective areas (3 CCR section 6452).

## **Regulatory Standards and Considerations**

Title 3, CCR section 6452 sets different standards by which to evaluate whether a new fumigation method will be allowed, one for the Sacramento Metro and South Coast ozone NAAs and one for the San Joaquin Valley, Southeast Desert, and Ventura ozone NAAs. Sacramento Metro and South Coast have a less stringent standard because no further VOC reductions from pesticides are needed in these ozone NAAs. Both "low-emission" and "high-emission" methods can be used in these two areas. Only "low-emission" methods are allowed in the San Joaquin Valley, Southeast Desert, and Ventura ozone NAAs during the May–October peak ozone season. The key information is the emission rating (percent of the fumigant applied that is emitted to the air) and the emission rate (emission rating multiplied by the maximum application rate). Either the emission rating or the emission rate can be no greater than the current methods allowed within the ozone NAAs by the regulations. The following table shows the standard for approval of an interim method for MITC, based on DPR's current emission estimates.

<b>Ozone Nonattainment Area</b>	<b>Maximum Allowed MITC Emission Rating (percentage)</b>	<b>Maximum Allowed MITC Emission Rate (pounds/acre)</b>
Sacramento Metro, South Coast	77	140
San Joaquin Valley, Southeast Desert, Ventura	28	51

In assessing whether the new method meets the standard, DPR must assess the scientific data submitted to establish the emission rating, normally consisting of field monitoring data. In evaluating this data, 3 CCR section 6452 requires DPR to consider the following factors:

- whether the information is sufficient to estimate emissions.
- whether the results are valid as indicated by the quality control data.
- whether the conditions studied represent agricultural fields.

### **Summary and Evaluation of the Submitted Information**

The Responsible Farmers Coalition submitted the study entitled “Field Volatility of MITC After Application of Metam-Sodium by Chemigation and Shank Injection Comparing Standard Water Sealing and Pulsed Water Sealing” by Dr. David Sullivan and Dr. Husein Ajwa, dated October 18, 2007, to support its request to allow metam-sodium applications at night. Dr. Sullivan and Dr. Ajwa measured the MITC emissions for two metam-sodium fumigation methods: shallow injection using tractor shanks and chemigation using sprinklers. All applications were initiated on July 26, 2007, between 1:00 a.m. and 2:00 a.m., and completed between 1:45 a.m. and 6:00 a.m. In addition to the two fumigation methods, Dr. Sullivan and Dr. Ajwa measured emissions from “standard” water treatments (continuous water application) and “pulsed” water treatments (alternating periods of water and no water application). Two water treatments were applied for all four applications, one immediately after application and the second during the evening of the day of application. All four applications were approximately 2.5 acres in size, separated by 900-1,600 feet, located in Kern County, and with metam-sodium applied at 75 gallons/acre (320 pounds active ingredient/acre). Using a combination of integrated horizontal flux and off-site back-calculation techniques, Dr. Sullivan and Dr. Ajwa estimated the following emissions for MITC over the four-day study period (emission rating and emission rate):

- night sprinkler with two pulsed water treatments: 37.65 percent and 67 pounds/acre.
- night sprinkler with two standard water treatments: 35.68 percent and 64 pounds/acre.
- night shallow injection with two pulsed water treatments: 2.22 percent and 4.0 pounds/acre.
- night shallow injection with two standard water treatments: 2.10 percent and 3.7 pounds/acre.

The report submitted on October 18, lacked some key information. DPR requested additional information in November 2007 and received it in December 2007. After several more phone calls and e-mail exchanges, DPR staff had a final discussion with Dr. Sullivan and Dr. Ajwa on February 13, 2008, and the last requested information was received on February 15, 2008.

DPR's scientific review of the report describes several shortcomings, both with the design and execution of the study. The most critical issues include:

- uncertainty of the air concentrations due to nonlinear calibration curves for the laboratory instrument.
- uncertainty of the air concentrations due to variable recoveries (28–175 percent) of samples containing known amounts of MITC (spiked samples).
- sampling halted when sprinklers were running.
- uncertainty in the emissions for some periods due to an insufficient number of valid samples or air concentrations that increased with height.

Additional work by the study authors or review of additional information by DPR would not further resolve these issues. Even with these shortcomings, many of the results are reasonably consistent with the results from other studies, particularly for the sprinkler application. While not preferred by the scientific staff, it is possible with a reasonable amount of certainty to set an upper-bound for the emission rates that will not be exceeded for these application methods. The attached memorandum contains the detailed review.

## **Findings**

The information provided, particularly the quality control data, indicates high uncertainty with the exact emissions for these fumigation methods. However, DPR staff is confident that the emissions are no greater than other fumigation methods currently in use. Therefore, DPR has assigned the following emission ratings to these methods:

- MITC night shallow injection method: 28 percent (based on current shallow injection method with two post-fumigation water treatments).
- MITC night sprinkler method: 77 percent (based on current sprinkler method with one post-fumigation water treatment).


## **Conclusions**

The emission ratings and the current maximum application rate of 320 pounds per acre of metam-sodium and 350 pounds per acre of metam-potassium support approval of these fumigation methods. Effective May 1, 2008, the MITC night shallow injection method is approved for use in all five ozone NAAs. Effective May 1, 2008, the MITC night sprinkler

method is approved for use in the Sacramento Metro and South Coast ozone NAAs, but not the San Joaquin Valley, Southeast Desert, or Ventura ozone NAAs during May–October. These fumigation methods may be used anytime outside of ozone NAAs and within any ozone NAA outside the May–October period, consistent with all VOC fumigation method restrictions.

In addition, the fumigation method descriptions and photographs for the shallow injection method show significant differences from the methods currently described in the regulations. Growers and applicators fumigating with the night shallow injection method must follow the regulatory recommendations for equipment and procedures described in part VI of the attached memorandum.

DPR grants interim approval of these fumigation methods for three years from the effective date. Due to the high uncertainty of the emission estimates, continued use of these fumigation methods beyond three years is contingent on the submittal of an additional acceptable study to more accurately document the emissions. Since DPR must adopt regulations to include these new methods prior to the expiration of the interim approval, the additional study should be submitted within 12 months. The additional study should include a comparison of the shallow injection method used for this study and the typical shallow injection method previously monitored (as described in the series of studies by D.L. Merricks in 1999, 2001, and 2002). DPR recommends that the Responsible Farmers Coalition submit a draft protocol for DPR scientific staff review prior to initiating the study.

By:  for \_\_\_\_\_  
Mary-Ann Warmerdam, Director  
Department of Pesticide Regulation

Date: 2/29/08

Attachment



# Department of Pesticide Regulation



Mary-Ann Warmerdam  
Director

## MEMORANDUM

Arnold Schwarzenegger  
Governor

TO: Randy Segawa  
Environmental Program Manager I  
Environmental Monitoring Branch

FROM: Pamela Wofford  
Senior Environmental Scientist  
Environmental Monitoring Branch  
(916) 324-4297

*Original signed by*

DATE: April 23, 2008

SUBJECT: AMENDMENT TO REVIEW OF "FIELD VOLATILITY OF METHYL ISOTHIOCYANATE AFTER APPLICATION OF METAM-SODIUM BY CHEMIGATION AND SHANK INJECTION COMPARING STANDARD WATER SEALING WITH PULSED WATER SEALING"

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In a memorandum to you dated February 26, 2008, Terrell Barry, Shifang Fan, and I described a review of a study on the emissions of methyl isothiocyanate from two metam-sodium fumigation methods: night shank injection with two water treatments and night sprinkler application with two water treatments. We mistakenly described part of the configuration of the application tractor used for the shank injection portion of the study. The compaction equipment was described as:

"The application tool bar(s) are followed by a ring roller with four gauge wheels controlled by hydraulic cylinders to control depth and or pressure to seal the chisel trace that is as least as wide as the application tool bar. The ring roller will be followed with a coil packer that is as least as wide as the application tool bar."

The compaction equipment and recommended permit conditions should instead be described as

"The application tool bar(s) are followed by a ring roller with four gauge wheels controlled by hydraulic cylinders to control depth and or pressure to seal the chisel trace that is as least as wide as the application tool bar, or a coil packer that is as least as wide as the application tool bar."





# Department of Pesticide Regulation



Mary-Ann Warmerdam  
Director

## MEMORANDUM

Arnold Schwarzenegger  
Governor

TO: Randy Segawa  
Environmental Program Manager I  
Environmental Monitoring Branch

FROM: Terrell Barry, Ph.D., Research Scientist III  
Environmental Monitoring Branch

*Original signed by*

Shifang Fan Ph.D., Environmental Scientist  
Environmental Monitoring Branch

*Original signed by*

Pamela Wofford, Senior Environmental Scientist  
Environmental Monitoring Branch  
(916) 324-4297

*Original signed by*

DATE: February 26, 2008

SUBJECT: REVIEW OF "FIELD VOLATILITY OF METHYL ISOTHIOCYANATE AFTER APPLICATION OF METAM-SODIUM BY CHEMIGATION AND SHANK INJECTION COMPARING STANDARD WATER SEALING WITH PULSED WATER SEALING"

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### I. Background

This field study had two main objectives: (1) measure flux from night metam sodium applications, and (2) compare evening watering-in that is applied over a two hour period with pulsed watering-in applied over a four hour period (30 minutes on/30 minutes off).

The original report did not contain enough detail to fully review the results. For example, the on-field mast measured air concentrations are shown in a plot but not in a table. In addition, the flux calculations were not included. Subsequently the authors submitted for review the quality assurance/quality control (QA/QC) data collected for the study and the spreadsheets and calculations used to estimate the flux for both methods. A review of those data is included in this memorandum.

This is the first night time shank application study submitted. In addition, the application rig is significantly different from the typical rig used in California. The applicator has submitted photographs and the rig specifications to the Department of Pesticide Regulation (DPR) for review. Before night shank applications using this rig are allowed, a second study should be conducted to verify that the emissions are reliably as low as those measured in this study since the results are so different from previous shank application method results. The additional study should include both the application rig used in this study (Western Farms rig) and the typical application rig used in the Merricks studies (Merricks, 1999; Merricks, 2001; Merricks, 2002).



Due to considerable uncertainty in the laboratory QA/QC and irregularities in the fieldwork (both discussed in detail below), it should be assumed that emissions for this new rig are the same as the typical rig. However, the typical rig used for metam sodium applications should not be allowed for night applications.

When differences in timing of the application are considered the sprinkler results are reasonably similar to the previous sprinkler results. The flux and concentrations are high during the night application. These results do not support allowing night sprinkler applications unless mass loss in the context of the volatile organic compound (VOC) regulations includes a large uncertainty factor. Acute exposure and buffer zones to protect persons off-site are not addressed in this review. Concentrations and flux decreases during the day and first the evening. As observed in previous studies, the intermittent watering-in performed early the first evening damps the increase in flux and air concentrations that has been observed for metam in standard watering-in studies. These results indicate that the total mass loss of approximately 37% for the sprinkler application method used in this study is less than the standard day sprinkler method (77%) but more than the intermittent watering-in day sprinkler application (28%). Uncertainty in the quality of these results infers a mass loss larger than the 37% estimated in this study.

Detailed review of the laboratory QA/QC and the fieldwork are presented separately below.

## **II. Laboratory Quality Assurance and Quality Control Comments**

This part of the review is focused on quality measures of methyl isothiocyanate (MITC) monitoring. During review, we had telephone, e-mail and a teleconference call exchanges with the University of California, Davis laboratory to obtain more detailed information concerning the laboratory analysis.

QA/QC measures for field samples included 12 duplicate samples at one sampling station, triplicates of field blank, and triplicates of trip spikes and field spikes each of three levels. QA/QC measures for laboratory analysis included determination of the detection limit as 2 µg/sample and 44 lab spike samples prepared by adding 10 µl of 10.8 µg MITC/µl of a standard fortification solution to the middle of the charcoal tube on the day the field samples arrived in the laboratory. The spiked tubes were stored, extracted and analyzed the same as the field samples. One laboratory spike was analyzed with every ten field samples. Based on the revised protocol for MITC analysis, these laboratory spikes were used “as standard QC/QA to confirm MITC storage stability on charcoal, extraction efficiency, and the GC measurement accuracy.”



DPR has seven major concerns about the laboratory practices:

1. Spiked samples at different concentrations should have been analyzed prior to the study to validate the gas chromatograph/mass spectrometry (GC/MS) method used for this study. According to e-mail communication: "the laboratory has been running MITC analyses following the Morse protocol using the NP detector since 2002, the GC/MS used for this study is a new GC purchased early last year. The laboratory used this GC because it was not expected that the concentrations were much lower than previous studies." The laboratory spikes mentioned above could not serve as analytical method validation since all spikes were at one concentration level of 108 µg MITC/tube. Standard laboratory practice is three to seven different levels for analytical method validation studies to cover concentration ranges of field samples. The reported results of field samples in this study ranged from 1 to 160 µg/tube.
2. A trapping efficiency study should have been conducted. The field spikes might provide information for trapping efficiency; however they were sampled in the field for only four hours and the results of the field spikes were highly variable. The field samples ran from three to eight hours.
3. The results of the single concentration laboratory spikes show a declining trend with analysis sequence (Figure 1). This indicates a systematic bias that increases over time.
4. The field QA/QC samples showed variable results and indicate possible problems. The results of field blank samples ranged from 0 to 0.87 µg/tube. Positive field blanks indicate a contamination problem. Recoveries of several trip spikes were high, ranging from 84.4% to 174.8%. Plus, these are inconsistent with the field spike results that showed low recoveries, ranging from 27.7% to 109%.
5. The laboratory standard calibration curves used to calculate the sample results were not linear ( $R^2=0.9793$ ) (Figure 2). For side-by-side comparison, a typical standard calibration curves ( $R^2=0.9997$ ) from the California Department of Food and Agriculture's laboratory is shown in Figure 3. Using a linear model for the nonlinear calibration curve leads to incorrect sample concentration results, particularly at low concentrations.
6. There is an inconsistency in MITC air concentrations between the data on page 77 of Sullivan Environmental Consulting, Inc.'s report and the data DPR calculated using the laboratory analysis results. Via e-mail communications, it turned out that the inconsistency was due to a subtraction of 0.6 µg/ml (6 µg/tube) from all analysis results including both on-field and off-field samples. This subtraction of 0.6 µg/ml was based on the average of differences between the results calculated by subtracting the y-intercept versus those calculated by forcing the slope through zero for the on-field samples. The differences of each

paired data ranged from -4.38 to 0.96 µg/ml. The investigators made these adjustments in an attempt to correct the nonlinear problems of the calibration curve discussed in number 5. DPR does not believe that either forcing the slope through zero or subtracting 6 ug/tube is an appropriate adjustment for this problem. In addition, making both adjustments appears to double-correct the results, underestimating the true concentrations. Attempting any recalculation of the results at this time is problematic.

7. One of purposes of this study was to compare MITC emission from different application methods, chemigation versus shank injection and standard water sealing versus pulsed water sealing. However, all samples of chemigation were analyzed in one period (July 31, 2007, 15:38 to August 1, 2007, 11:03) and results were calculated using one standard curve (calibration slope); all samples of shank injection were analyzed in another period (August 1, 2007, 15:44 to August 3, 2007, 3:10) and results were calculated using a different standard curve (calibration slope). This sample analysis schedule may introduce systematic errors that would confound comparison of different application methods.

The following are specific comments on the different documents:

On Revised Protocol:

1. Page 1, the paragraph of Stock Solution, the last sentence: This stock solution should contain 0.995 mg MITC /ml since the purity is 99.5%.
2. Page 2, the first paragraph: Either the concentration unit of the spiking standard or the procedure was wrong. If following the procedure, the spike standard solution concentration should be 10 µg/ml, not 10 µg/µl. Also the purity of the MITC analytical standard should be considered.
3. Page 2, the paragraph of Field Sample Fortification: If following the procedure that 10 µl of 0.05, 1.0, and 20 µg/ml MITC standard solutions was spiked, the fortified tubes should have contained 0.0005, 0.01, and 0.2 µg/tube MITC, not 0.5, 10, and 200 µg/tube. It is possible that the concentration unit of the spiking solutions was wrong.

On Report:

1. Page 33, the median values were used for field spike recovery values, 95.2 to 109.2%. With only three samples, a range should have been reported instead of the median.
2. Page 35, the last sentence: it is unclear how the 2 µg/tube was converted to 20 µg/m<sup>3</sup>. With a flow rate of 1 liter/minute, the sampling time would be only 100 minutes. However, most samples ran approximately 200-500 minutes.

3. Page 36, the analytical standard purity, date of expiration, and certificate of analysis were documented in the laboratory files: except for the purity provided in revised analysis protocol, other information was not provided anywhere.

Laboratory spreadsheet:

1. In the on-field sample sheet, all dup A1 should be dup B1.
2. Two sets of data were the same, but labeled differently. One set were the results in the columns of P, Q, and R of each worksheet of the Laboratory spreadsheet\_MITC\_7\_07\_Bakersfield.xls file. Via phone conversation, these results were from the 10 ppm of the standard solution for continuous standard calibration control (as in page 36 of the report). The other set of data was actually collected from all the results on the P, Q, and R of each worksheet of the Laboratory spreadsheet\_MITC\_7\_07\_Bakersfield.xls file and listed on the Standard fortified laboratory samples worksheet of the MITC-stds.xls file as the results of the laboratory spike samples analyzed with every 10 field samples.

### III. Fieldwork Comments

**Page 14. First Paragraph.** This paragraph states that for the evening watering-in periods on-field samplers were not run when the sprinklers were running. While this is reasonable to avoid damage to the samplers, the study design should have been planned to have sufficient off-site samplers to provide a back-calculated estimate of the flux. It is completely unknown how much mass loss was missed due to the lack of samplers during the irrigation events. In addition, the pump running times for the standard watering-in treatments are not clear. The field history sheets are difficult to decipher.

**Page 28. Chemigation Plots (#1 and #2).** This paragraph states that Plot #2 was completed at 10:40 a.m. However, Table 2 indicates that the initial watering-in was finished at 0800 hours. It is unclear whether the 10:40 a.m. refers to the completion of setting up the sonic anemometer tower rather than the watering-in.

**Page 29. First paragraph.** This paragraph states that Appendix F contains confirmatory results for periods 3-6. However, Appendix F shows only figures and the heading of Appendix F “Confirmatory Modeling versus Measured Plots (Periods 4-6)” is in conflict with the caption of the very first plot where it states that the plot is for Period 3. These sorts of mistakes lead to doubt about the correctness of the remainder of the report.

**Page 29. Last paragraph.** The irrigation paragraph indicates that the irrigation was quite variable with the shank applications receiving less water than the planned amount. The authors end by saying that if the irrigation is averaged *across fields* that results were generally close to

design amounts. However, the authors also provide unsupported speculation that if the shank applications had not received 14% to 21% less water than planned that the shank results would show even lower emissions. So, the author's statements are in conflict. Either the average amount across fields is acceptable and the variation is judged to not be significant or the shank received significantly less, not both.

**Page 34. Tables 7 and 8.** Field Fortifications, Blanks, and Duplicates.

The authors conclude that the field blank and duplicate results are acceptable. However, the Field Spike results are quite variable, showing recoveries between 28% and 175%. The Field Blanks are contaminated. The Duplicates are not in as close agreement as inferred in the text—for the range of concentrations observed in most samples in this study the duplicates differ by an average 12%.

**Pages 35–36. Table 9.** This table indicates that recoveries for samples with 0.5 ug/tube are acceptable. Yet on Page 35 the text states that, based upon Merricks (1999), any on-field tubes with 2 ug/tube or less were defaulted to a “flux value” of  $<1 \text{ ug/m}^2/\text{sec}$ . The flux and the results should use all observations above the detection limit for this laboratory (University of California, Davis) and this study.

**Page 37. Section 3.0.** This section states that Appendix C contains tabular results of all on-field and ambient measured concentrations. First, Appendix C is not labeled as such. Second, no off-site air concentrations are shown in what appears to be Appendix C. Third, the off-site air samples are not ambient samples by DPR definition. Ambient samples are taken to characterize regional sub-chronic and chronic exposures. The samples taken in this study represent acute exposures and are simply off-site air concentrations.

**Page 37–50. Section 4.0.** Section 4.2—the flux is estimated by back-calculation, not the “ambient method.”

**Page 43, 44, and 79.** The shank emission profile analysis shows 13 of the 18 periods where the air concentration profile does not behave according to the assumption of decreasing air concentrations with height. The air concentrations for most of these 13 periods are similar to the lower concentrations in the sprinkler emission profiles. However, with the exception of the last sampling interval, the sprinkler emission profiles do show decreasing air concentrations with height. It is noted in review of the laboratory QA/QC that all the sprinkler samples were analyzed together over several days followed by all the shank samples analyzed together days later. This can lead to systematic laboratory differences that confound results. It cannot be ruled out that this occurred in these laboratory analyses and the emission profiles may illustrate that problem. Specifically, in the figures on Page 79, there are times when the 3 ft or 1 ft samples show air concentrations higher than the 0.5 ft sampler or when the 1 ft sampler shows an air concentration higher than the 3 ft sampler. The key sampling period for the shank method on

field 4 (Period 2), estimated flux with only 2 samples. This is not acceptable. In future studies the on-site air concentrations should be measured at more than three levels for the IHF method. That way if one sampler is lost the results will still be acceptable. Most IHF studies in the literature use at least 5 measurement heights.

**Page 47. Figure 14A.** These results seem suspect. For the shank fields the “upwind” air concentrations are higher than the on-site concentrations. In addition, the shank on-site air concentrations are substantially lower than sprinkler onsite concentrations but the “upwind” samplers for shank and sprinkler show concentrations of similar magnitude. It makes no sense that off-site air concentrations are higher than those measured on-site (see page 89). This may indicate laboratory problems and/or cross-field plot contamination. These field plots were much closer than DPR would advise and the potential for cross-field contamination is significant (see page 92). The authors may have justified the orientation and spacing of these field plots based on consulting prevailing wind patterns in the area. However, prevailing winds mean nothing when measuring air concentrations over more than a few hours. This study was conducted over four days.

**Page 49. Section 4.6 and Figure 15.** The percent of MITC emitted results shown in Figure 15 were checked using the flux estimates for each sampling interval provided by the authors in an Excel spreadsheet. The exact mass loss calculations for all four fields were not provided so it was difficult to verify the results shown in Figure 15. The recalculated mass loss estimates were slightly different from that shown in Figure 15. There appears to be two reasons for the differences: (1) the authors used a conversion of 4.2 pounds of metam sodium per gallon of product rather than the label conversion of 4.26 pounds per gallon and (2) it appears that the authors used a uniform 75 gallons per acres application rate for all four applications to calculate the percent loss. However, both shank applications received less than 75 gallon per acres. Thus, the sprinkler mass loss estimates are virtually identical due to the very small difference between 4.2 and 4.26 lbs metam sodium per gallon product and the shank estimates differ slightly due to both the pounds metam sodium per gallon difference and the difference in total mass applied.

Although comparisons of the sprinkler mass loss results with previous sprinkler studies is difficult, the results do seem reasonable based upon trends in those previous studies. Comparisons between the results from the sprinkler application in this study and the night application studies in DPR database, Wofford (1994) and Sullivan (2006), are difficult because the timing of the applications were significantly different. The Wofford application was started at 1940 hours on August 3, so, the entire application, the watering-in and several hours after were under dark hours. This would lead to substantial mass lost, 73.3% loss was observed through the first night. The Sullivan (2006) study application was started at 0400 hours and completed after sunrise. The first watering-in was applied during daylight hours. Total mass loss in Sullivan (2006) was 39.1%. The applications in this report were started at 0100 hours and Table 2

indicates that the watering-in was completed at 0800 hours. This means that the period following the watering in was during daylight. The additional watering-in on the first evening would be expected to further reduce the loss. The Wofford loss through the watering-in was 53%, for Sullivan (2006) loss through the initial watering-in was 10%. Total loss for this study was about 37% with a loss through initial watering-in of approximately 13%.

These shank loss results are not consistent with any of the shank results DPR already has. The shank application mass loss result in this study is substantially less than any of the previous shank studies. In fact, these shank mass losses are similar to the drip application losses observed in Levine et al. (2005), and Li et al. (2006). DPR has no other night shank application data. Other than the change in rig, nothing in the report indicates reasons for the extremely small mass loss. These extremely low mass loss estimates for night shank application should be verified with a second trial before DPR uses these results for VOC calculations.

**Page 51. Conclusions.** Each conclusion is discussed below:

1. Shank injection/compaction . . .produced excellent retention of MITC . . .

This conclusion cannot be made until the QA/QC issues are resolved. Unfortunately, it is not likely laboratory QA/QC issues can be completely resolved.

2. Relatively small differences were observed between the pulsed and continuous water seals for chemigation.

These results seem internally consistent. It is unlikely corrections for the QA/QC would change this conclusion.

3. The use of on-field profiles and the integrated horizontal flux method produced a high degree of precision . . .

The authors are placing importance on precision to the exclusion of accuracy. The precision of these results is unimportant if the accuracy is unacceptable. Even the precision is at issue due to the significant QA/QC issues.

4. In order to quantify very low levels of emissions . . .

See comments on the detection limit above. There is conflicting information relating to the detection and quantification limits.

5. Nighttime applications based on shank injection . . .well managed off-gassing rates.

This conclusion cannot be made until the QA/QC issues are resolved. Unfortunately, it is not likely laboratory QA/QC issues can be completely resolved.

6. Nighttime applications using chemigation would benefit by modified water sealing practices in order to better retain MITC in the heat of the day . . .

A field study would need to demonstrate that this additional water application would significantly reduce the loss. The first two sampling intervals, as expected, showed the highest flux. If the results are taken as they are, the loss in this study is similar to Sullivan (2006).

#### **IV. Discussion**

Previous studies (Merricks, 1999; Merricks 2001, and Merricks 2002) have indicated that total mass loss for sprinkler and shank are similar. This study shows widely differing results between sprinkler and shank. The shank applications would be expected to show the same increase in flux during the day that was shown by the sprinkler. However, measured air concentrations for shank were so low that no trend was demonstrated. A second study should be conducted to confirm that the new rig is the reason for the very low emission obtained for shank. Period 2 (the critical period) shank flux was estimated using only two points. A simple straight line was fit to characterize the concentration profile because one of the three samples was lost. This, in addition to the considerable uncertainty in the laboratory QA/QC cast significant doubt on the shank results.

#### **V. Technical Recommendations**

There are two alternatives regarding the data in this report:

1. Reject the report due to laboratory QA/QC issues and irregularities in the field study conduct. This is most defensible from a scientific standpoint and our preference.
2. Use the mass loss results but add uncertainty factors to the results. The recommended uncertainty factors for the VOC program only are as follows: (a) assume the sprinkler mass loss is the same as standard sprinkler, and (b) assume the shank mass loss is the same as intermittent shank. Acute exposure of persons off-site is not addressed in this review. These results are not of sufficient quality to allow an assessment of required acute exposure buffer zones for these methods. Use of this alternative is a completely qualitative management decision.

Regardless of which alternative is chosen above, because the shank mass loss reported in this study is substantially less than losses observed in any prior shank study, a second field study

should be conducted to confirm these results. The second study should directly compare the standard shank method to the Western Farm rig used in this study.

## **VI. Regulatory Recommendations**

If a nighttime application is to be allowed, it must adhere to the specifications used in the application studies. Therefore, the following regulatory requirements are recommended for these fumigation methods:

### **For Night Sprinkler Application with Two Post-Fumigation Water Treatments**

- the field must receive an initial irrigation at a rate of 0.20 inches immediately prior to application
- the application period must be initiated no earlier than 0100 hrs and be applied at a minimum rate of 0.20 acre-inches/hour
- post-fumigation water treatments must be consistent with the requirements described in Title 3, California Code of Regulations, section 6450.1(d)(2)\*

### **For Night Shank Application with Two Post-Fumigation Water Treatments**

- application must start no earlier than 0100 hours
- post-fumigation water treatments must be consistent with the requirements described in Title 3, California Code of Regulations, section 6450.1(d)(2)\*
- the following fumigation equipment and procedures must be used
  - i. Before application, thoroughly cultivate the field to remove clods with a disc or spring tooth bar. Soil must contain adequate moisture (as stated in regulations) prior to application
  - ii. The application equipment must meet the following criteria:
    - The shanks must be set on a single or multiple bars so there is an effective spacing of no more than 4 inches between shanks.
    - Injection depth is 3 inches, 6 inches, and 9 inches.
    - Nitrogen must be used to purge the system before applicator bar is lifted out of the ground at any time.

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\* The 0.20 inches for the post-fumigation water treatments described in the regulations should be changed to 0.40 inches, so it is consistent with the water treatments for this and previous monitoring studies



iii. Compaction equipment

The application tool bar(s) are followed by a ring roller with four gauge wheels controlled by hydraulic cylinders to control depth and or pressure to seal the chisel trace that is as least as wide as the application tool bar.

The ring roller will be followed with a coil packer that is as least as wide as the application tool bar.

**New Method Codes for Field Fumigation Methods**

Since both application methods are new, the following will be used for the fumigation code on the Pesticide Use Reporting and the Field Fumigant VOC Emission Allowance forms:

Method code	Emission Rating (%)	Regulation Section Field Fumigation Method
1452	77	6452 (b)(1) Night Sprinkler/Broadcast or Bed/ Two Water Treatments
1455	28	6452 (b)(1) Night Nontarpaulin/Shallow/Broadcast or Bed/ Two Water Treatments

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Figure 1. Recoveries of the laboratory spikes in analysis sequence

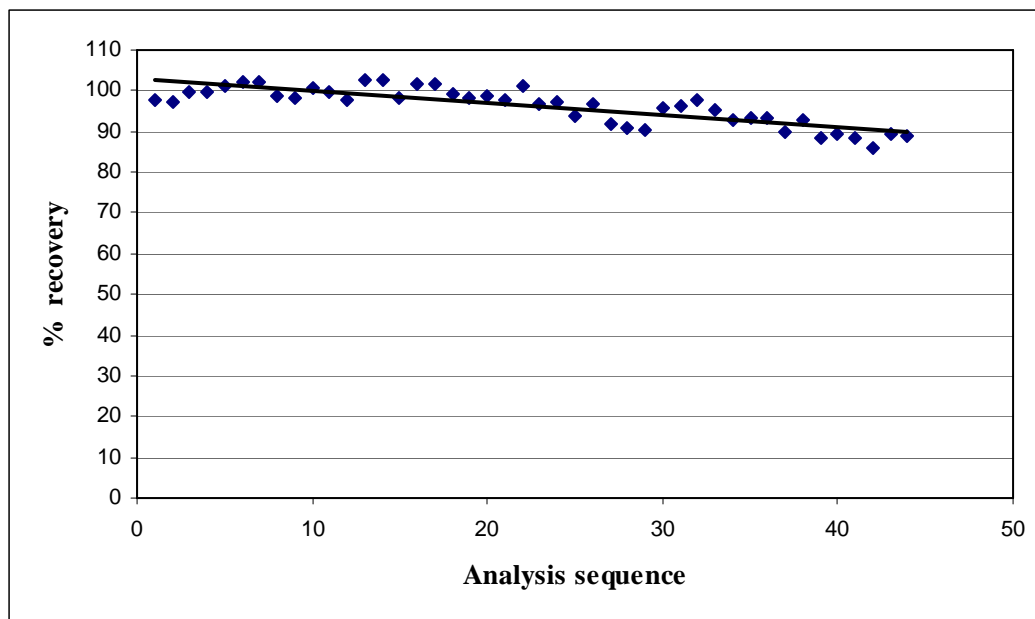
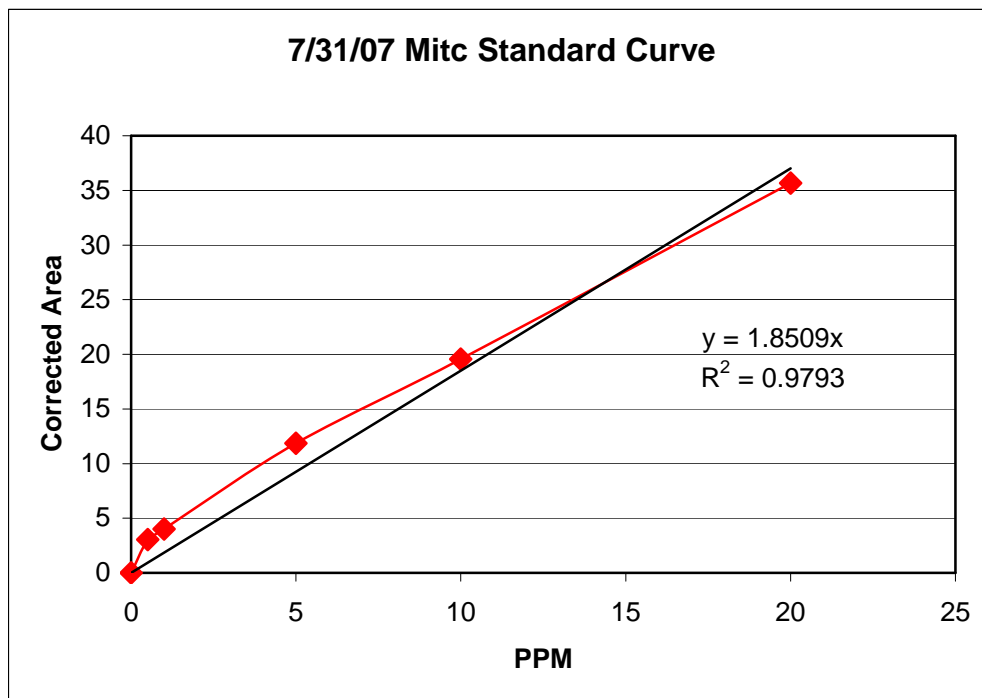


Figure 2. One copy of standard curves for laboratory analysis data calculation in Bakersfield study, 2007



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Figure 3. A typical MITC standard curve from the California Department of Food and Agriculture's laboratory analysis

